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**APPLICATION OF SOLID STATE SENSOR
FOR QUANTITATIVE MEASUREMENT OF HYDROGEN
IN SOUR C PIPELINES**

by

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ABSTRACT

The results of a series of experiments to assess the performance of amperometric sensors and a potentiometric sensor for monitoring hydrogen in a commercial steel pipeline, are reported.

The equivalent pressure of hydrogen p_{H_2} in the steel determined by the potentiometric sensor on exposure to standard corroding solutions saturated with hydrogen sulphide at 1 atm, 25°C, is $p_{H_2} = 1000 \times 10^{-1.0pH}$. The diffusion coefficient of hydrogen in the steel ($4.9 \times 10^{-7} \text{ cm}^2/\text{s}$) determined by the potentiometric sensor, agrees with values determined by the amperometric sensors.

Introduction

Pipeline steels in sour gas service are prone to hydrogen induced cracking (HIC) or stepwise cracking (SWC). Susceptibility of a steel to this phenomenon depends upon metallurgical factors and environmental factors. Important metallurgical factors are the presence of alloying elements, microstructure, segregation and shape of non-metallic inclusions. Important environmental factors are the pressures of hydrogen sulphide and carbon dioxide, temperature, pH of the medium and the presence of aggressive ions such as chloride. Many failures of pipeline containing sour gas have been reported which have been attributed to HIC.

Experimental work at CANMET⁽¹⁾ identified two parameters contributing to HIC:

1. Threshold hydrogen concentration in the steel: the concentration of diffusible hydrogen above which HIC occurs.
2. Threshold pH: the solution pH below which HIC occurs.

The threshold pH was used to rank the steels with respect to HIC resistance.

There is a need for a sensor to give warning of high hydrogen concentration in the pipeline steel of industrial installations. Two types of sensor, attached to the external surface of the pipeline, are available:

1. Amperometric sensors which measure the equivalent flux of hydrogen through the steel, from which the hydrogen concentration at the inner surface of the steel pipe may be estimated.
2. Potentiometric sensors which measure the equivalent hydrogen gas pressure in the steel.

An experimental programme to assess the merits of the two types of sensor was recently completed at the CANMET laboratories. This report is primarily concerned with the performance of the potentiometric sensor. Some comparisons with data derived from the amperometric sensors are made.

Theory

The constructional details of these two types of sensors have been described in the literature^(2,3) and need not be discussed here. The amperometric sensor depends upon electrochemical oxidation of hydrogen diffusing through the steel. The measured current, I is equivalent to the hydrogen flux, J through the steel,

$$J = \frac{I}{2FA} \quad (1)$$

where A is the surface area and F is the Faraday. The elapsed time between initiation of the hydrogen flux at the inner surface and response of the sensor (the breakthrough time, t_b) enables calculation of the diffusion coefficient D of hydrogen in the steel⁽⁴⁾,

$$D = \frac{\ell^2}{15.3 t_b} \quad (2)$$

where ℓ is the thickness of the steel. Assuming D is independent of hydrogen concentration in the steel, the concentration at the inner surface, c_{Hi} , may be calculated:

$$c_{Hi} = \frac{J\ell}{D} \quad (3)$$

It may be noted that the amperometric sensor utilizes an aqueous solution of sodium hydroxide as electrolyte. This needs periodical replacement.

The potentiometric sensor is a solid state electrochemical cell utilizing Nafion (DuPont Inc) polymer electrolyte in conjunction with a reference electrode comprising Fe^{II} and Fe^{III} sulphate hydrates. The cell voltage E is related to the hydrogen pressure p_{H_2} at the sensing electrode by the Nernst equation,

$$p_{\text{H}_2} = \exp \left[\frac{2F}{RT} (E - E^\circ) \right] \quad (4)$$

where E° is a constant and R , T have their usual meaning. E° is determined by calibration of the sensor with pure hydrogen gas at 1 atm. The sensor also permits determination of D by equation 2. In principle, with the sensor mounted on steel, the measurement of E and the calculation of p_{H_2} (eq. 4) permits determination of the concentration of hydrogen, c_{H} in the steel. In general the relationship between c_{H} and p_{H_2} for commercial steels is not known; hence c_{H} cannot be calculated at present. An experimental programme to determine this relationship is in progress at the University of New Brunswick.

It may be noted that the potentiometric sensor requires no maintenance.

Experimental

The sensors were strapped to the external surface of a specimen of commercial steel pipeline (~15.2 cm dia., 0.72 cm thickness) inside which a standard solution, saturated with hydrogen sulphide (1 atm. pressure) was placed. The properties of the steel are summarized in Table 1. The standard solutions were de-aerated with nitrogen and saturated with hydrogen sulphide prior to placement in the steel pipe at time zero. A new specimen of the steel pipe was used for each of the four experiments conducted with standard corroding solutions of different pH. A flat was milled on the external surface of the pipe for mounting the potentiometric sensor. The wall thickness of the pipe at the minimum was 0.62 cm. A smear of silicone grease was applied to the interface between the sensing electrode and the steel surface prior to mounting.

The current, from the amperometric sensors, and the voltage, from the potentiometric sensor, were measured as a function of time. Experiments were conducted at ambient temperature $\sim 25^{\circ}\text{C}$, in the sequence of standard corroding solution pH, 2.8, 3.5, 5.4 and 4.2.

Results and Discussion

The voltage - time charts obtained from the potentiometric sensor for the four test solutions of pH = 2.8, 3.5, 4.2 and 5.4 are presented in figs 1 to 4. Key features of the charts, the breakthrough time, t_b , and the maximum voltage E_{max} are summarized in Table 2 together with the calculated diffusion coefficient D (eq. 2) and the equivalent hydrogen pressure (eq. 4, with $E^{\circ} = 0.656\text{V}$).

It is seen from figs 1 to 4 that the voltage-time profiles are similar with some variations for solutions of higher pH. The low initial voltages (-0.3 to -0.4V) recorded for three of the four tests are consistent with the presence of oxygen at the sensing electrode. This has been verified by calibration tests of the sensor with oxygen gas⁽³⁾.

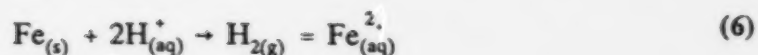
The diffusion coefficient of hydrogen in the steel determined from the four tests (see Table 2) is $4.9 \pm 0.5 \times 10^{-7} \text{ cm}^2/\text{s}$. The values of D determined from two tests with the amperometric sensors were 4.7×10^{-7} and $7.9 \times 10^{-7} \text{ cm}^2/\text{s}$. These results are in reasonable agreement.

The equivalent hydrogen pressures noted in Table 2 are well defined from E_{max} with the exception of data from test 3 (fig 3) at pH = 4.2. In this case a peak voltage (0.66V) was followed by a rapid decline to $\sim 0.59\text{V}$. A plot of $\log p_{\text{H}_2}$ vs solution pH for tests 1, 2 and 4 gives the regression equation,

$$\log p_{\text{H}_2} = -1.05 (\text{pH}) + 3.09, r = \sim 1.0 \quad (5)$$

At pH = 4.2, $\log p_{\text{H}_2} = -1.32$ (eq 5) and $E = 0.62\text{V}$ (eq 4) close to the mean of the values noted above for this test. It is clear from these data that the equivalent hydrogen pressure in the steel increases with increasing hydrogen concentration (decreasing pH) in the test solution.

The trend of $\log p_{\text{H}_2}$ with pH noted above may be understood qualitatively by consideration of the overall corrosion reaction,



A thermodynamic calculation predicts the equilibrium hydrogen gas pressure to be $\sim 10^{14}$ atm at pH = 2.8 and $\sim 10^9$ atm at pH = 5.4. The increased equivalent hydrogen pressure determined by the sensor at the lower solution pH must be a reflection of the thermodynamic driving force of the corrosion reaction.

Conclusions

1. The solid state potentiometric sensor is responsive to hydrogen in steel.
2. The equivalent hydrogen pressure p_{H_2} in the commercial steel used in the experiments is related to the pH of the corroding solution, saturated with hydrogen sulphide at 1 atm pressure, 25°C by the expression,

$$p_{\text{H}_2} = 1000 \times 10^{-1.0 \text{ pH}}$$

within the limits of experimental error.

3. The diffusion coefficient of hydrogen in the commercial steel, determined from the breakthrough time with the potentiometric sensor is $4.9 \pm 0.5 \times 10^{-7} \text{ cm}^2/\text{s}$. This value agrees well with the diffusion coefficient determined from the breakthrough times observed with the amperometric sensors.

Table 1. Composition of Commercial Steel
CANMET Designation: G3

Element	wt %	Element	wt %
C	0.095	Sn	<0.005
Mn	0.855	Al	0.04
P	0.013	Nb	0.01
Si	0.21	B	0.0001
Ni	0.165	Cu	0.165
Mo	<0.005	Cr	0.03
Ca	0.0039	S	0.001
Ti	<0.005	V	<0.005

Table 2. Summary of Data from Potentiometric Sensor

Fig No.	Test Solution Code*	pH	t_b s	E_{max} V	D cm^2/s	P_{H_2} atm
1	TM0177	2.8	48×10^3	0.66	5.2×10^{-7}	1.4
2	CSA	3.5	52×10^3	0.64	4.8×10^{-7}	0.29
3	TM0284	4.2	47×10^3	0.66-0.59 (0.625 mean)	5.3×10^{-7}	0.089
4	TM0284	5.4	62×10^3	0.58	4.1×10^{-7}	0.003

*TM0177 and TM0284 are NACE standard solutions

CSA: Canadian Standards Association

References

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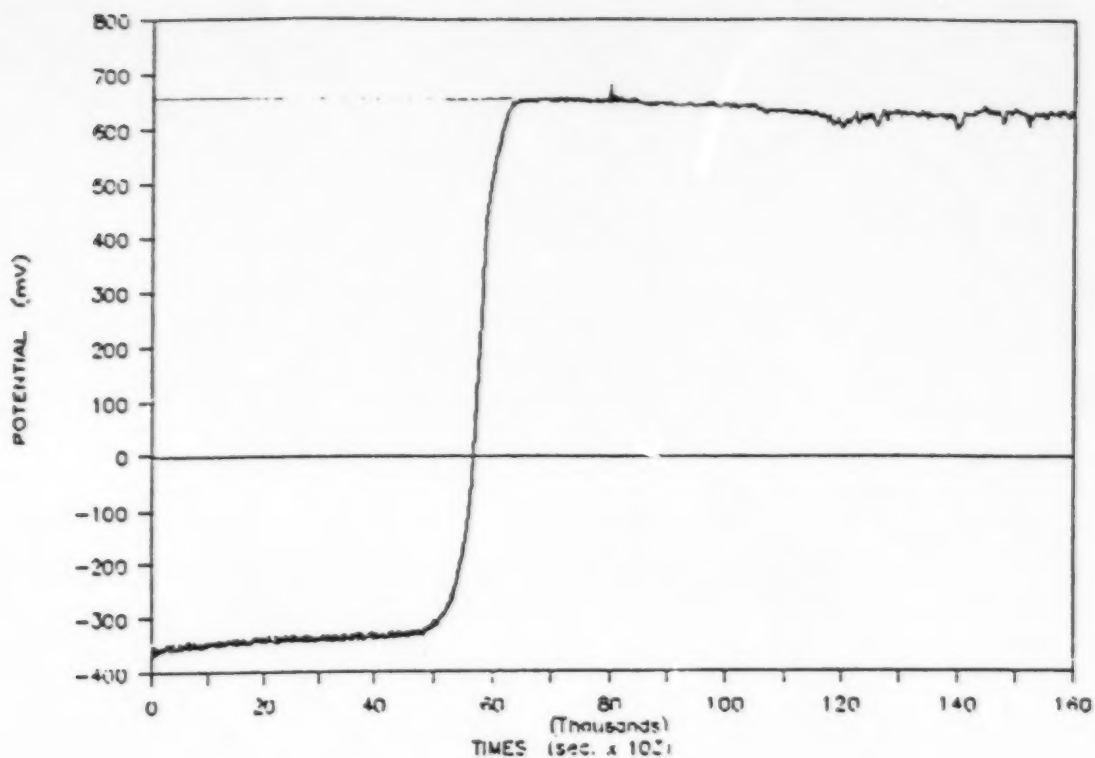


Fig 1. Response of Potentiometric Sensor
Test Solution: TM0177, pH = 2.8

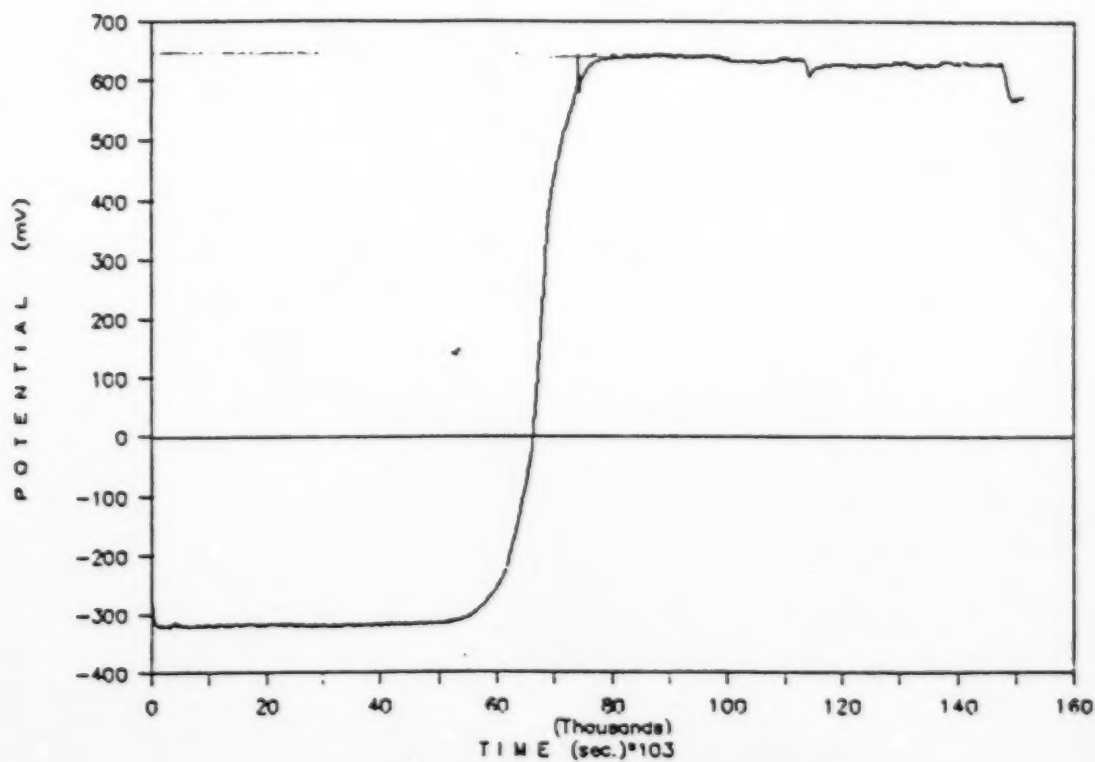


Fig 2. Response of Potentiometric Sensor
Test Solution: CSA, pH = 3.5

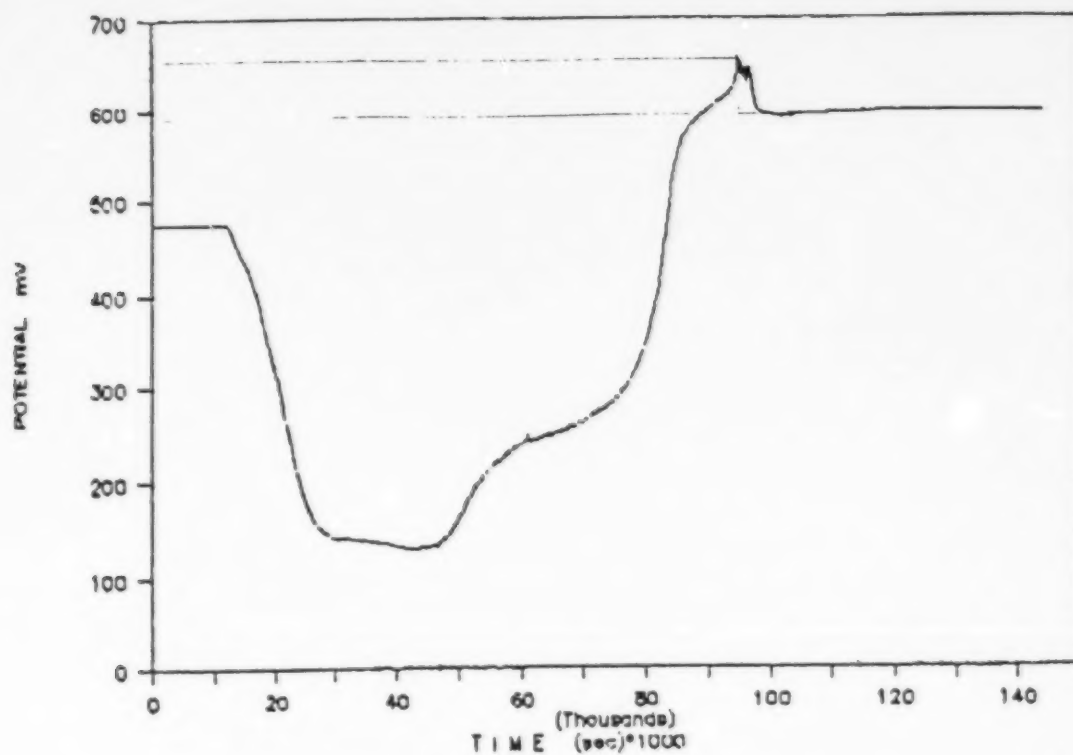


Fig 3. Response of Potentiometric Sensor
Test Solution: TM0284, pH = 4.2

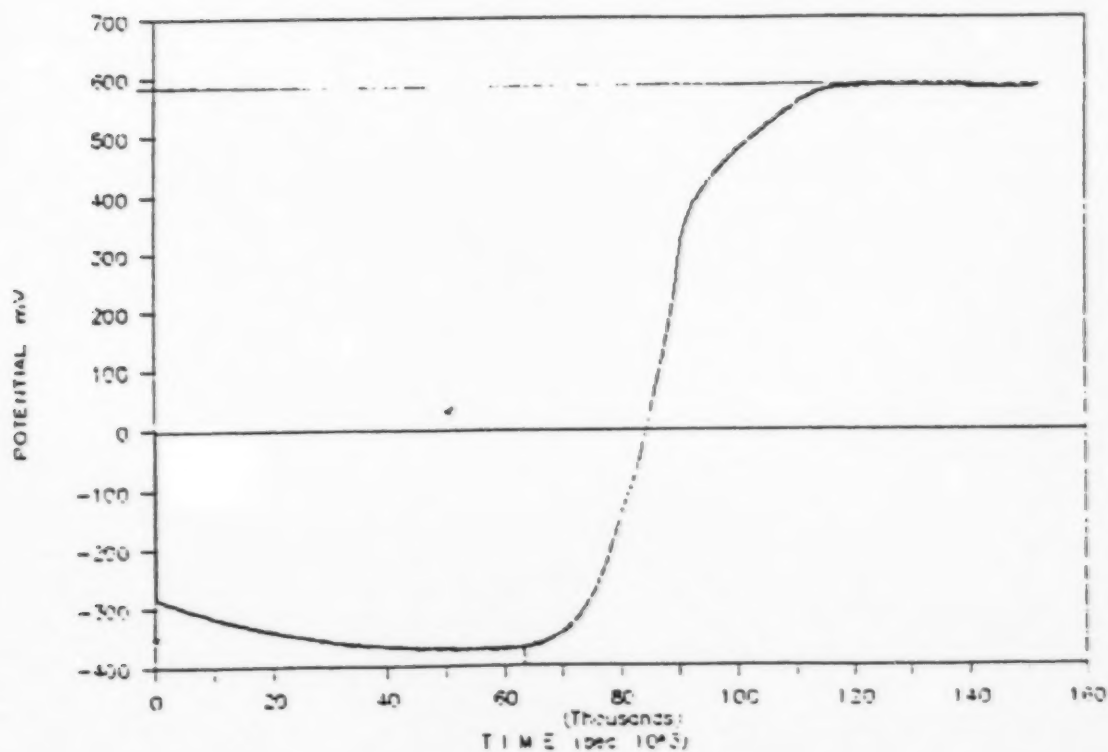


Fig 4. Response of Potentiometric Sensor
Test Solution: TM0284, pH = 5.4